

Organic matter in space - An overview

Ewine F. van Dishoeck^{1,2}

¹Leiden Observatory, Leiden University
P.O. Box 9513, NL-2300 RA Leiden, the Netherlands
email: ewine@strw.leidenuniv.nl

²Max-Planck Institute für Extraterrestrische Physik, Garching, Germany

Abstract. Organic compounds are ubiquitous in space: they are found in diffuse clouds, in the envelopes of evolved stars, in dense star-forming regions, in protoplanetary disks, in comets, on the surfaces of minor planets, and in meteorites and interplanetary dust particles. This brief overview summarizes the observational evidence for the types of organics found in these regions, with emphasis on recent developments. The *Stardust* sample-return mission provides the first opportunity to study primitive cometary material with sophisticated equipment on Earth. Similarities and differences between the types of compounds in different regions are discussed in the context of the processes that can modify them. The importance of laboratory astrophysics is emphasized.

Keywords. Astrochemistry, molecular data, circumstellar matter, methods: laboratory, comets: general, minor planets, ISM: abundances, ISM: molecules, infrared: ISM, stars: AGB and post-AGB

1. Introduction

Organic matter is defined as chemical compounds containing carbon-hydrogen bonds of covalent character, i.e., with the carbon and hydrogen forming a true chemical bond. Observations over the last century have established that these molecules are ubiquitous throughout the universe, not only in our Galaxy (Kwok 2007b) but even out to high redshifts (Yan *et al.* 2005). With the detection of more than 200 exoplanetary systems, a major question is whether these organic compounds can be delivered in tact to new planetary systems where they could form the basis for the origin of life. The answer requires a good understanding of the entire lifecycle of organic molecules from their formation in the outflows of evolved stars to the diffuse interstellar medium (ISM) and subsequently through the star-forming clouds to protoplanetary disks. Ehrenfreund & Charnley (2000) and Ehrenfreund *et al.* (2002) summarized our understanding of this cycle several years ago, but since then new observations (e.g., with the *Spitzer Space Telescope*), laboratory experiments, and in-situ space missions (in particular the *Stardust* mission) have occurred. Thus, a symposium such as this reviewing these recent developments is timely.

In this opening paper, a broad overview will be given where organic matter is found in space and which species have been identified. Subsequently, observational evidence of how and where these molecules are modified will be summarized. Finally, a number of questions to address at the symposium and in the future are raised. The importance of laboratory astrophysics in providing the basic data to interpret astronomical and solar-system observations and analyse meteoritic and cometary samples is emphasized.

2. The need for laboratory astrophysics

Several decades ago, Henk van de Hulst accused cosmologists of ‘playing tennis without a net’, when they were putting forward many models that could not be tested by any observations. Similarly, much of astrochemistry (and, in fact, much of astronomy as a whole) would be ‘playing tennis without a net’ if there were no laboratory data available to analyse and interpret the observational data of astronomical sources. The list of required data for organic compounds is extensive, and getting such information for even a single molecule often involves the building up of sophisticated laboratory equipment followed by years of painstaking data taking.

The most basic required information is spectroscopy of organic molecules from UV to millimeter wavelengths to identify the sharp lines and broad bands observed toward astronomical sources. One recent development in this area is the use of cavity ringdown spectroscopy to increase the sensitivity compared with classic absorption spectroscopy by orders of magnitude, which has allowed measurements of rare species that can be produced only in small amounts. Examples include gaseous polycyclic aromatic hydrocarbons (PAH) (e.g., Tan & Salama 2005, Rouille *et al.* 2007) or carbon chains (e.g., Dzhonson *et al.* 2007, Linnartz *et al.* 2000), in addition to matrix-isolation studies of large samples of PAHs (e.g., Hudgins & Allamandola 1999). Spectroscopy data bases of solids, including silicates (e.g., Jaeger *et al.* 1998, 2003), carbonates (e.g., Posch *et al.* 2007), ices (e.g., Bisschop *et al.* 2007a, Bernstein *et al.* 2005) and carbonaceous material (e.g., Mennella *et al.* 1997, Jaeger *et al.* 2006, Muñoz-Caro *et al.* 2006) continue to grow.

The next step in understanding organics is to obtain rates for the various reactions that are expected to form and destroy organics under space conditions. Here recent developments include measurements and theory of gaseous neutral-neutral rate coefficients at low temperatures (e.g., Chastaing *et al.* 2001, Smith *et al.* 2006), branching ratios for dissociative recombination (e.g., Geppert *et al.* 2004), and rates for photodissociation of molecules exposed to different radiation fields (van Hemert & van Dishoeck 2008). Surface science techniques at ultra high-vacuum conditions are now being applied to study thermal- and photo-desorption (e.g., Collings *et al.* 2004, Öberg *et al.* 2007) and formation of simple organic ices at temperatures down to 10 K (e.g., Watanabe *et al.* 2004, Bisschop *et al.* 2007b), while more traditional set-ups continue to provide useful information on the formation of complex organics in ices exposed to UV (e.g., Elsila *et al.* 2007, Muñoz-Caro & Schutte 2003) and to higher energy particle bombardment (e.g., Hudson & Moore 2000). There is also a wealth of new literature on the formation of carbonaceous material in discharges (e.g., Imanaka *et al.* 2004) and its processing at higher temperatures and when exposed to UV (e.g., Dartois *et al.* 2007).

Finally, the techniques to analyze meteoritic and cometary material in the laboratory have improved enormously in the last decade, and now allow studies of samples on submicrometer scale. Examples include ultra-L²MS and nano-SIMS (e.g., Messenger *et al.* 2007), XANES (e.g., Flynn *et al.* 2006) and NMR (e.g., Cody *et al.* 2005). Their development was essential for analysis of the samples returned by *Stardust*.

3. Which organic compounds are found where?

In the following sections, the observational evidence for organic material is summarized, together with the identification of the type of material, where possible (Figure 1). For small gas-phase molecules, the identification is unambiguous, but for larger compounds often only the types of carbon bonds making up the material can be specified. Carbon can be bonded in several ways: a triple CC bond with single H on the side (e.g.,

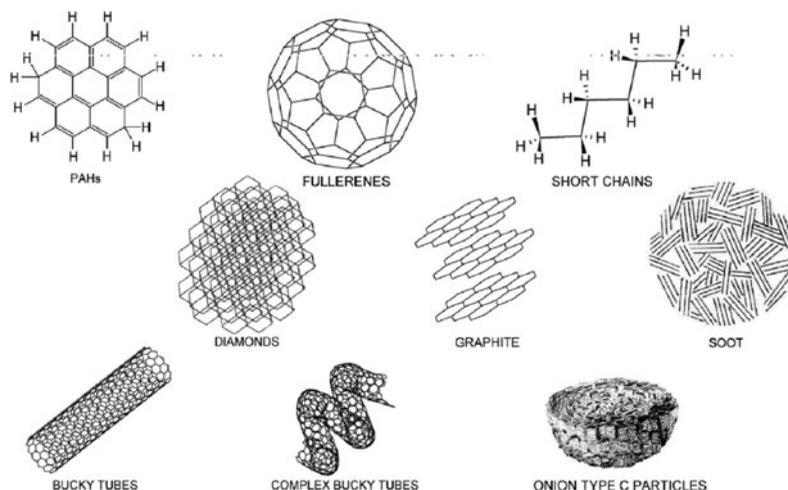


Figure 1. Examples of different types of carbonaceous material which are likely present in the ISM and Solar System (from: Ehrenfreund & Charney 2000)

$\text{HC}\equiv\text{CH}$, denoted as sp hybridization); a double CC bond with two H's on each side (e.g. $\text{H}_2\text{C}=\text{CH}_2$, denoted as sp^2 hybridization) and a single CC bond with three H's on each side (e.g., $\text{H}_3\text{C}-\text{CH}_3$, denoted as sp^3 hybridization). In aromatic material, the electrons are delocalized over the entire molecule such as in a benzene ring or a polyethylene chain with alternating double and single CC bonds. The molecule thus contains sp^2 bonds. In aliphatic material, no double bonds occur, and only sp^3 hybridization is found. Spectral signatures of organic compounds include strong electronic transitions at optical and UV wavelengths, vibrational transitions at infrared wavelengths, and pure rotational transitions at millimeter wavelengths. In the latter case, the molecule needs to have a permanent dipole moment to be detected.

The majority of carbon in interstellar clouds (at least 50%) is in some form of carbonaceous solids with grain sizes large enough ($\sim 0.1 \mu\text{m}$) not to have any clear spectroscopic signature, other than continuous opacity. Another fraction of the carbon (up to 30%) can be in gaseous C, C^+ and/or CO, or in CO and CO_2 ices. Most of the discussion in this paper concerns the remaining $\sim 20\%$ of carbon present in carbonaceous molecules, ices and small grains.

3.1. Diffuse and translucent clouds

Diffuse and translucent molecular clouds are concentrations of the interstellar gas with extinctions up to a few mag (for review, see Snow & McCall 2006). Typical temperatures range from 15–80 K and densities from a few $100\text{--}1,000 \text{ cm}^{-3}$. These are the only types of clouds for which high quality optical and UV spectra can be obtained by measuring the electronic transitions in absorption against bright background stars. In addition to the simplest organics CH, CH^+ and CN detected in 1937–1941, a series of more diffuse features called the ‘diffuse interstellar bands’ (DIBs) has been known since 1922. Nearly 300 DIBs are now known in the $4,000\text{--}10,000 \text{ \AA}$ range (e.g., Hobbs *et al.* 2008), but not a single one has yet been firmly identified despite numerous suggestions by the world's leading spectroscopists. Two bands at 9577 and 9632 \AA are consistent with features of C_{60}^+ , but laboratory spectroscopy of gaseous C_{60}^+ is needed for firm identification of the first fullerene in interstellar space (Foing & Ehrenfreund 1997). Long carbon chains with $n < 10$ and small PAHs have been excluded (Maier *et al.* 2004, Ruiterkamp *et al.* 2005),

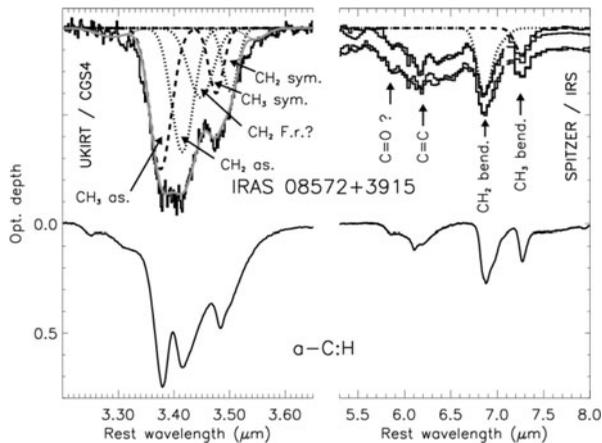


Figure 2. *Spitzer* and ground-based IR spectrum toward the galaxy IRAS 08572+3915 compared with a laboratory spectrum of amorphous carbon a-C:H. The spectrum in the 5–8 μm range excludes large amounts of O- and N- containing groups. It suggests a larger ratio of aliphatic over aromatic content than thought before (Dartois *et al.* 2007).

but larger versions are possible. The amount of carbon locked up in the DIB carriers is likely small, $< 1\%$, assuming typical oscillator strengths for large molecules.

Measurements of the UV extinction curve show a bump at 2175 \AA , characteristic of the $\pi \rightarrow \pi^*$ transition in carbonaceous material. The precise identification is still uncertain, with both graphitic and hydrogenated amorphous carbon (HAC, a material consisting of islands of aromatic C joined by a variety of peripheral sp^2 - and sp^3 -bonded hydrocarbons) leading candidates (e.g., Draine 2003). A major puzzle is why no DIB features have yet been seen at UV wavelengths, since small carbon-bearing molecules should have strong electronic transitions in this region.

At IR wavelengths, the characteristic ‘unidentified infrared bands’ (UIR) bands are seen in emission throughout the diffuse ISM, even in clouds exposed to the normal interstellar radiation field (see review by Tielens 2008). The commonly accepted identification is with PAHs of sizes small enough ($N_C \approx 50$) to be excited by UV and emit in discrete bands. It is clear that the fraction of O and N in PAHs is very low, but a small amount of N (few % w.r.t. carbon) has been proposed to explain the small shift of the interstellar 6.2 μm feature compared with laboratory data of pure PAHs (Hudgins *et al.* 2005). Alternative explanations include the presence of small side chains (Sloan *et al.* 2005). The fraction of carbon locked up in small PAHs is estimated to be $\sim 4\%$. Large PAHs or PAH clusters may be responsible for the plateaus underlying the discrete PAH bands, containing of order 2% of the carbon, whereas the Very Small Grains (VSGs) responsible for the 12 μm IRAS emission contain a similar amount (Tielens 2008).

In lines of sight which sample large columns of diffuse gas (e.g., toward the Galactic center, external galaxies), a feature at 3.4 μm has been seen (see review by Pendleton 2004). This wavelength is characteristic of the stretching modes of $-\text{CH}_2$ and $-\text{CH}_3$ groups in aliphatic material (Duley & Williams 1983). Many materials have been proposed, ranging from HAC to Quenched Carbonaceous Composites (QCC), Kerogen (a coal-like material consisting of arrays of aromatic carbon sites, aliphatic chains and linear chains of benzenic rings) and photoprocessed carbon-containing ices. New constraints come from *Spitzer* observations of the 5–8 μm region (Dartois *et al.* 2007) (Figure 2). The absence of strong CO and CN bands points again to little N and O, but the $-\text{CH}_2$ and $-\text{CH}_3$ bending modes are clearly seen and can be well fitted by a HAC or a-C:H (amorphous

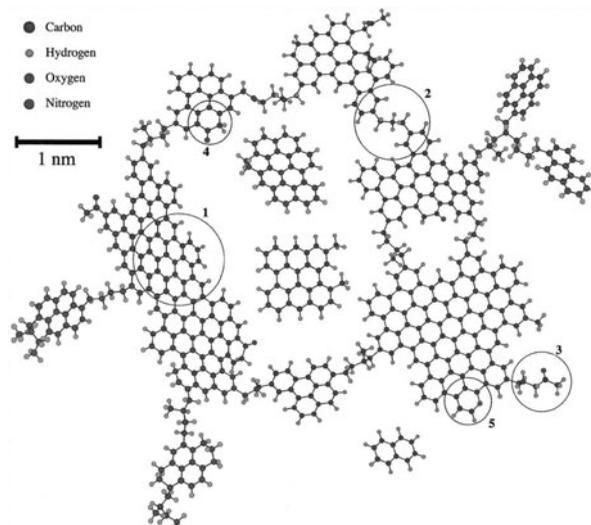


Figure 3. Proposed structure of the carbonaceous interstellar dust in the diffuse ISM by Pendleton & Allamandola (2002). The structure is a kerogen-type aromatic network bridged by aliphatic chains, including side groups and hetero-atoms. A typical $0.1 \mu\text{m}$ carbonaceous grain would contain $\sim 10^4$ of these fragments. One of the challenges for this meeting is to determine whether this picture is still valid, or whether, for example, more aliphatic chains have to be added.

carbon) material, which typically contains about 15% of the available carbon. A possible representation of the carrier of the $3.4 \mu\text{m}$ feature is presented in Figure 3.

Finally, small carbonaceous molecules like C_3H_2 have been detected in absorption at mm wavelengths toward distant quasars whose line of sight passes through a galactic molecular cloud (Lucas & Liszt 2000). These molecules are also seen in emission in Photon-Dominated Regions (PDRs) with abundances that are much higher than expected from standard ion-molecule reactions. One possible explanation is that they result from photodissociation of larger carbonaceous molecules such as PAHs (Pety *et al.* 2005).

3.2. Evolved stars

The spectra of carbon-rich (proto-)planetary nebulae (PPN) are full of IR emission features, with both the aromatic PAH and the aliphatic $3.4 \mu\text{m}$ bands commonly observed in emission (e.g., Goto *et al.* 2007). Interestingly, the aromatics are stronger and aliphatics weaker in planetary nebulae (PN) compared with earlier evolutionary stages. Also, they appear to be larger than in the diffuse ISM, with $N_C \approx 100 - 200$. In the AGB phase leading up to the extreme carbon stars, C_2H_2 absorption at $13.7 \mu\text{m}$ (the building block to make benzene) and emission features at 21 and $30 \mu\text{m}$ are seen, with the latter two still unidentified (see overview by Kwok 2007a).

A particularly interesting object is the Red Rectangle, a protoplanetary nebula which shows prominent Extended Red Emission (ERE), both as a continuum at $5,000-7,000 \text{ \AA}$ and in discrete bands (van Winckel *et al.* 2002). Some of the latter are close to the positions of strong DIBs seen in diffuse clouds. The positions and shapes of both the IR and optical bands may vary with distance from the star, suggesting a change in the composition of the material with UV dose (Song *et al.* 2003).

3.3. Dense star-forming regions

Cold dense cores are the realm of the long unsaturated carbon chains such as HC₉N, discovered in the 1970's. Recent developments include the identification of negative ions such as C₆H⁻ and C₈H⁻ (McCarthy *et al.* 2006) as well as more saturated chains such as CH₂CHCH₃ (Marcelino *et al.* 2007). Taken together, these chains make up only a small fraction, < 0.1%, of the total carbon budget.

Saturated complex organic molecules such as CH₃OH, CH₃OCH₃ and C₂H₅CN are commonly seen in high abundances toward warm star-forming regions such as Orion and Sgr B2, which have been surveyed at (sub)mm wavelengths for more than 30 years (e.g., Schilke *et al.* 2001). Such 'hot cores' have been detected around most massive protostars and are now commonly used as a signpost of the earliest stages of star formation. One recent development is that they are also found around low-mass protostars, with IRAS 16293–2422 as the prototypical example (Cazaux *et al.* 2003). Abundance ratios from source to source are remarkably constant (e.g., Bisschop *et al.* 2007c, Bottinelli *et al.* 2007) pointing to an origin in grain surface chemistry, although some variations between low- and high-mass sources are found. Also, a clear segregation of oxygen- and nitrogen-rich organics is seen (e.g., Wyrowski *et al.* 1999). One of the major questions is whether all observed complex organics are produced in the ice or whether some of them are formed in the hot gas following evaporation of ices (Charnley *et al.* 1992). Each organic molecule has an abundance of typically 10⁻⁹ – 10⁻⁷ with respect to H₂, but the total fraction of carbon locked up in these complex molecules can amount to a few %.

More complex organic molecules such as amino acids and bases, which are relevant for pre-biotic material, have not yet firmly been identified. Indeed, the spectra of hot cores are so crowded that line confusion is a serious issue. Ethylene glycol, CH₂OHCH₂OH, a complex organic found in comets, has been claimed in Sgr B2 (Hollis *et al.* 2002), but its detection is not yet fully secure.

The largest reservoir of volatile carbonaceous material is in the ices, whose strong mid-infrared absorption bands are seen not only toward most massive protostars (Gibb *et al.* 2004) but also toward a wide variety of low-mass YSOs (e.g., Boogert *et al.* 2008). Besides H₂O ice, CO, CO₂, OCN⁻, CH₄, HCOOH, CH₃OH and NH₃ ice have been identified. The recent surveys of low-mass YSOs show that some molecules like CH₄ have relatively constant abundances of ~ 5% with respect to H₂O ice (Öberg *et al.* 2008), whereas those of CH₃OH vary from < 1 to 25% (see Bottinelli *et al.*, this volume). Altogether, the known organic molecules (excluding CO and CO₂) may lock up to 10% of the available carbon.

Most significant is the absence of PAH and 3.4 μm emission or absorption in the cold cores and deeply embedded stages of star formation. Indeed, a recent *Spitzer* and VLT survey of low-mass embedded YSOs shows no detections, indicating PAH abundances that are at least a factor of 10 lower than in the diffuse gas, perhaps due to freeze-out (Geers *et al.* 2008). No absorptions due to PAHs in ices have yet been found, but the lack of basic spectroscopy prevents quantitative limits.

3.4. Protoplanetary disks

Once the collapsing cloud has been dissipated, a young star emerges which can be seen at visible wavelengths but is still surrounded by a protoplanetary disk. PAH emission has been detected in roughly half of the disks surrounding Herbig Ae stars, i.e., intermediate mass young stars (Acke & van den Ancker 2004). More recently, PAHs have also been seen in a small fraction (~ 10%) of disks around solar mass T Tau stars (Geers *et al.* 2006). A quantitative analysis of the emission indicates PAH abundances that are typically factors of 10–100 lower than in the diffuse ISM, either due to freeze-out or caused by

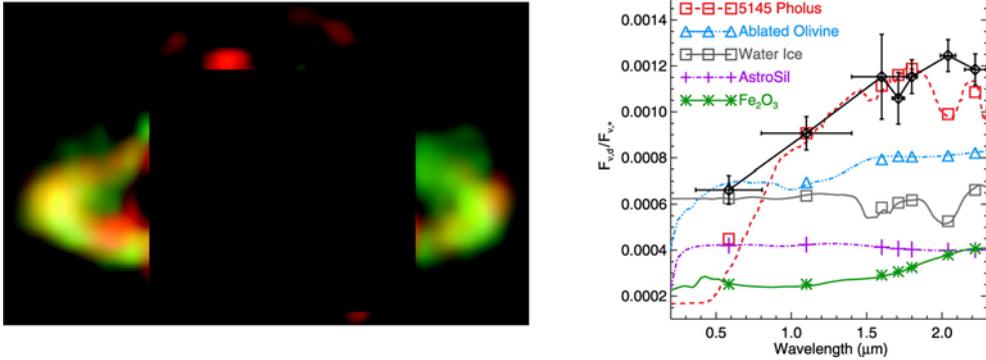


Figure 4. Left: False color HST image ($\sim 4'' \times 4''$) of the HR 4796A disk. Blue corresponds to $0.58 \mu\text{m}$, green to $1.10 \mu\text{m}$ and red to $1.71 \mu\text{m}$. Right: Disk / stellar flux ratio as function of wavelength. For comparison, grain models for candidate materials with a $n^{-3.5}$ size distribution with $a_{\text{min}} = 3 \mu\text{m}$ and $a_{\text{max}} = 1,000 \mu\text{m}$ are shown, normalized to the $1.10 \mu\text{m}$ data for HR 4796A and offset for clarity (from: Debes *et al.* 2008).

coagulation. The spatial extent of the PAH emission measured with adaptive optics on 8 m class telescopes is of order 100 AU, i.e., comparable with the size of the disk, but varying with feature (Habart *et al.* 2004). Modeling of the spatial extent as well as the destruction of PAHs by the intense UV or X-ray emission from the star indicates that the PAHs must be large, $N_C \approx 100$ (Geers *et al.* 2007b, Visser *et al.* 2007).

Smaller organics are present in high abundances in the inner disk (< 10 AU). Indeed, hot (400–700 K) C_2H_2 and HCN have been detected in absorption in edge-on disks with abundances factors of 1,000 larger than in cold clouds (Lahuis *et al.* 2006). Recently, they have also been seen in emission (Carr & Najita 2008). The observed abundances are consistent with models of hot dense gas close to LTE (e.g., Markwick *et al.* 2002).

A particularly intriguing class of disks is formed by the so-called transitional or ‘cold’ disks with large inner holes. An example is Oph IRS 48, in which a large (60 AU radius) hole is revealed in the large grain $19 \mu\text{m}$ image. Interestingly, PAHs are present inside the hole, indicating a clear separation of small and large grains in planet-forming zones (Geers *et al.* 2007a). Another intriguing case is formed by the more evolved disk around HR 4796A, which has likely lost most of its gas and is on its way to the debris-disk stage. Recent HST imaging shows colors with a steep red slope at $0.5\text{--}1.6 \mu\text{m}$ and subsequent flattening off (Debes *et al.* 2008) (Figure 4). These colors are reminiscent of those of minor planets in our Solar System, such as the Centaur Pholus, where the data are best fitted with tholins, i.e., complex organics produced in the laboratory in a CH_4/N_2 discharge with characteristics similar to Titan’s haze (e.g., Cruikshank *et al.* 2005).

3.5. Comets and minor planets

Many volatile organics have been detected in bright comets like Hale-Bopp thanks to improved sensitivity at IR and mm wavelengths (see reviews by Bockelée-Morvan *et al.* 2000, 2006). Most of them are parent species evaporating directly from the ices. The list includes HCN, C_2H_2 , C_2H_6 , CH_3OH , ..., all of which except C_2H_6 have also been detected in star forming regions in the ice or gas. Typical abundances are 0.1–few % with respect to H_2O ice. A larger variety of comets originating from both the Oort cloud and Kuiper Belt have now been sampled, and variations in abundances between comets are emerging, with organics like CH_3OH and C_2H_2 depleted by a factor of 3 or more in some comets

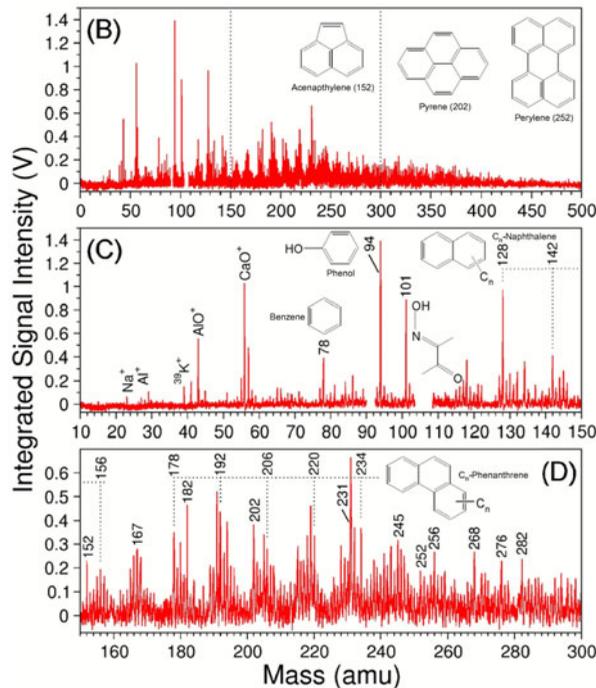


Figure 5. *ultra-L²MS* analysis of one of the *Stardust* samples, showing the presence of small PAHs (from: Clemett *et al.* 2007).

(e.g., Kobayashi *et al.* 2007). PAHs have not yet been firmly identified by ground-based $3.3\ \mu\text{m}$ spectra.

Fly-bys through the comae of Comets Halley, Borelly and Wild 2 have provided a much closer look at cometary material, including in-situ mass spectrometry of the gases. A major discovery of the *Giotto* mission to Halley was the detection of the so-called CHON particles: complex, mostly unsaturated, organics with only a small fraction of O and N atoms (Kissel & Krueger 1987).

A major question is whether the evaporating gases are representative pristine material unchanged since the comets were formed more than 4 billion yr ago, or whether they have been changed by ‘weathering’ (e.g., high-energy particle impact) during their long stay in the outer Solar System. The *Deep Impact* mission to Comet Tempel 1 was specifically designed to address this question, by liberating pristine ices from deep inside the comet following impact (A’Hearn *et al.* 2005). A significant increase in the IR emission around $3.5\ \mu\text{m}$, characteristic of CH_3CN and CH-X bands was seen immediate after impact, but no strong PAH bands were evident.

The *Stardust* mission has taken a major step forward in the study of primitive Solar System material by returning samples from Comet Wild 2 back to Earth, where they can be subjected to in-depth laboratory analysis using the most sophisticated experimental techniques (Brownlee *et al.* 2006). Wild 2 is a less evolved comet than others, having spent most of its lifetime in the Kuiper Belt and being captured into its current orbit only 30 years ago. Thus, it should not have suffered much thermal heating close to the Sun. Many complex organic molecules are found in the analysis of the *Stardust* particles to date, with a heterogeneous distribution in abundance and composition between particles. Many of the organics are PAHs, with typical sizes of just a few rings, i.e., generally smaller than the PAH size inferred in the ISM (Sandford *et al.* 2006, Clemett *et al.* 2007) (Figure 5).

Also, a new class of aromatic poor organic material is found compared with those seen in IDPs and meteorites, perhaps related to the fact that Wild 2 has had less thermal processing. The material appears richer in O and N than meteoritic organics. A major challenge for future studies will be to quantify the organics produced by the particle impacts inside the aerogel and isolate those from true cometary material.

Evidence for the presence of organics on other minor planets comes from their red colors at optical and near-IR wavelengths as seen in reflected sunlight. A particularly well studied case is the surface of the Centaur object Pholus (Cruikshank *et al.* 2005). Since discrete spectral features are lacking, identification of the material is not unique, but energy deposition in gas and ice mixtures containing CH₄ and N₂ produces tholins with colors similar to those observed (Imanaka *et al.* 2004).

Titan is particularly interesting because its atmosphere is thought to be similar to that of our (primitive) Earth, with the main difference being that it consists mostly of N₂ and CH₄ rather than N₂ and CO₂. The *Cassini* mission has studied Titan's haze in detail and the descent of the *Huygens* probe through the atmosphere has indeed revealed many nitrogen-rich organics (Niemann *et al.* 2005). Methane in the atmosphere must be continuously replenished by cryo-volcanism or other processes, since its lifetime due to photochemistry is short.

Besides tholins, HCN polymers have also been speculated to be part of the dark component present on outer Solar System bodies, including comets (Matthews & Minard 2006). It can also contribute to the orange haze in the stratosphere of Titan. Overall, it is clear that organics are a widespread component of Solar System material.

3.6. Meteorites and IDPs

The most primitive and least processed meteorites — the so-called carbonaceous chondrites — contain ample organic material. Well known examples are the Murchison, Orgueil and Tagish Lake meteorites, which contain up to 3% by weight in carbon-rich material. Most of the organics (60–80%) are in an insoluble macromolecular form, often described as 'kerogen-like'. The remaining 20% are in soluble form and have been found to contain carboxylic acids, PAHs, fullerenes, purines, amides, amides and other prebiotic molecules (e.g., Cronin & Chang 1993, Botta & Bada 2002). Amino acids — more than 80 different types — have also been found, but are likely formed from reactions of liquid water with HCN and H₂CO under the high pressure in the parent body rather than being primitive Solar System material.

Interplanetary dust particles (IDPs) have been collected through stratospheric flights over the past decade and analyzed in detail in the laboratory. Organic carbon, including aliphatic hydrocarbons and the carrier of the 2175 Å feature, are common (Flynn *et al.* 2000, Bradley *et al.* 2005).

4. Evolution of organic matter

As organic material evolves from the evolved stars to the diffuse and dense ISM, and subsequently from collapsing envelopes to disks, icy solar system bodies and meteorites, many processes can affect their composition and abundance (Ehrenfreund & Sephton 2006). From the AGB and PPN phase to the PN phase, UV processing changes aliphatics to aromatics material (Kwok 2007a). In the subsequent step, the organics can be shattered by shocks as they enter the diffuse ISM and are exposed to passing shocks from supernovae and winds (Jones *et al.* 1996). Destruction of graphite produces very small carbonaceous grains, including presumably the smaller PAHs. When the organics enter the dense cloud phase, freeze-out will affect all organics, coagulation can occur,

and the changing balance between UV dissociation and re-hydrogenation can modify the aliphatic to aromatic abundance ratio (e.g., Muñoz-Caro *et al.* 2001). Also, volatile complex organics are formed on the grains as ices.

Once the molecules enter the inner part of the collapsing envelope, ices will evaporate and some of the material is transported into disks, either as ice or gas. UV radiation and heating can further process the material before it becomes incorporated into cometary or planetary material. Here weathering and processing over the last 4.5 billion yr can change the top layers of the parent body, whereas aqueous alteration and thermal processing can further change the composition of organics in meteorites. Given all this potential processing, it is natural to expect the organics in the different sources to vary substantially.

4.1. *Similarities*

One of the strongest pieces of evidence that some organic material may remain unaltered through this entire cycle comes from the similarity of the 3.4 μm feature in the diffuse ISM and in meteorites (Pendleton 2004). Also, the mere presence of PAHs in (proto)planetary nebulae, the diffuse ISM, comets and meteorites suggests that these molecules are not fully destroyed during the lifecycle from evolved stars to solar systems.

Another intriguing piece of the puzzle is provided by the similarity in the composition and abundances of ices in protostellar regions and comets: is this just a coincidence or are the original ices preserved as they enter the comet-forming regions? The answer likely depends on the volatility of the species. Also, the similar red colors found in at least one protoplanetary disk and those seen on minor planets hint at preservation of the more refractory organics in the transport through disks. Finally, the presence of the 2175 Å bump in IDPs and in the ISM suggests a common carbonaceous carrier.

4.2. *Differences*

There is also abundant evidence that not all organics seen in the various sources are the same. The PAH and 3.4 μm aliphatic features are not seen in dense clouds or protostellar sources, with abundances of the carriers inferred to be lower by factors of 10–100, most likely due to freeze-out. Also, the sizes of PAHs in meteorites are smaller than those in the ISM and disks, which in turn are smaller than those found in (proto-)planetary nebulae. Aliphatic material is transformed into aromatics with increasing UV dose in evolved stars. Thus, most of the PAHs seen in protoplanetary disks are not the same as those seen around evolved stars.

In terms of volatiles, some large organics are clearly much more abundant in comets than in interstellar gases or ices, with ethylene glycol a good example. Organics in comets are also different compared with IDPs and meteorites, both in terms of PAHs and other species. This suggests processing during planetary formation or during the journey of the meteorites and IDPs to Earth.

5. Some open questions

The above summary raises many questions that should be addressed in this meeting and future studies. How is carbonaceous material formed in the envelopes of evolved stars and how does the composition depend on stellar parameters? What is the main form of solid carbon? How important is UV processing in modifying organic matter, or even producing it (e.g., from UV processing of water-poor ices)? How relevant are the volatile complex organics found in star-forming regions to the origin of life? Do they survive the transport from clouds to disks to planetary systems? What is the link between interstellar and Solar System refractory macromolecular carbon? Where do the CHON particles found

in comets fit in? How are the interstellar PAHs modified in disks, and where is the ‘soot’ line in relation to the terrestrial planet-forming zones?

The future is bright thanks to upcoming new observational facilities such as ALMA, further development of infrared interferometers, HST-COS, JWST and ELTs. Complementary laboratory work will be even more essential to make progress.

The author is grateful to S. Kwok for the invitation and hospitality. This work is supported by a Spinoza grant from NWO.

References

- Acke, B. & van den Ancker, M. E. 2004, *A&A*, 426, 151
- A’Hearn, M., *et al.* 2005, *Science*, 310, 258
- Bernstein, M. P., Cruikshank, D. P., & Sandford, S. A. 2005, *Icarus*, 179, 527
- Bisschop, S. E., Fuchs, G. W., Boogert, A. C. A., van Dishoeck, E. F., & Linnartz, H. 2007a, *A&A*, 470, 749
- Bisschop, S. E., Fuchs, G. W., van Dishoeck, E. F., & Linnartz, H. 2007b, *A&A*, 474, 1061
- Bisschop, S. E., Jørgensen, J. K., van Dishoeck, E. F., & de Wachter, E. B. M. 2007c, *A&A*, 465, 913
- Bockelée-Morvan, D., Crovisier, J., Mumma, M. J., & Weaver, H. A. 2006, in: M.C. Festou *et al.* (eds.), *Comets II*, (Univ. of Arizona), p. 391
- Bockelée-Morvan, D., *et al.* 2000, *A&A*, 353, 1101
- Boogert, A. C. A., *et al.* 2008, *ApJ*, 678, 985
- Botta, O. & Bada, J.L. 2002, *Surveys Geophys.*, 23, 411
- Bottinelli, S., Ceccarelli, C., Williams, J. P., & Lefloch, B. 2007, *A&A*, 463, 601
- Bradley, J., *et al.* 2005, *Science*, 307, 244
- Brownlee, D., *et al.* 2006, *Science*, 314, 1716
- Carr, J. S. & Najita, J. 2008, *Science*, 319, 1504
- Cazaux, S., *et al.* 2003, *ApJ* (Letters), 593, L51
- Charnley, S. B., Tielens, A. G. G. M., & Millar, T. J. 1992, *ApJ* (Letters), 399, L71
- Chastaing, D., Le Picard, S. D., Sims, I. R., & Smith, I. W. M. 2001, *A&A*, 365, 241
- Clemett, S., *et al.* 2007, *LPI*, 1338, 2091
- Cody, G. D. & Alexander, C. M. O. 2005, *Geochimica et Cosmochimica Acta*, 69, 1085
- Collings, M. P., *et al.* 2004, *MNRAS*, 354, 1133
- Cronin, J. R. & Chang, S. 1993, in: J.M. Greenberg *et al.* (eds.), *The chemistry of life’s origin*, (Dordrecht: Kluwer), p. 209
- Cruikshank, D. P., Imanaka, H., & Dalle Ore, C. M. 2005, *Adv. Space Res.*, 36, 178
- Dartois, E., *et al.* 2007, *A&A*, 463, 635
- Debes, J. H., Weinberger, A. J., & Schneider, G. 2008, *ApJ* (Letters), 673, L191
- Draine, B. T. 2003, *ARA&A*, 41, 241
- Duley, W. W. & Williams, D. A. 1983, *MNRAS*, 205, 67
- Dzhonson, A., Jochnowitz, E. B., & Maier, J. P. 2007, *J. Phys. Chem. A*, 111, 1187
- Ehrenfreund, P. & Charnley, S. B. 2000, *ARA&A*, 38, 427
- Ehrenfreund, P., Irvine, W., Becker, L., *et al.* 2002, *Rep. Prog. Phys.*, 65, 1427
- Ehrenfreund, P. & Sephton, M. A. 2006, *Faraday Discuss.*, 133, 277
- Elsila, J. E., Dworkin, J. P., Bernstein, M. P., Martin, M. P., & Sandford, S. A. 2007, *ApJ*, 660, 911
- Flynn, G. J., *et al.* 2000, *Bioastronomy* 99, p. 191
- Flynn, G. J., *et al.* 2006, *Science*, 314, 1735
- Foing, B. H., & Ehrenfreund, P. 1997, *A&A* (Letters), 317, L59
- Geers, V. C., Augereau, J.-C., Pontoppidan, K. M., *et al.* 2006, *A&A*, 459, 545
- Geers, V.C., Pontoppidan, K.M., van Dishoeck, E. F., *et al.* 2007a, *A&A* (Letters), 469, L35
- Geers, V. C., *et al.* 2007b, *A&A*, 476, 279
- Geers, V. C., *et al.* 2008, *A&A*, submitted
- Geppert, W. D., *et al.* 2004, *ApJ*, 613, 1302

- Gibb, E. L., Whittet, D. C. B., Boogert, A. C. A., & Tielens, A. G. G. M. 2004, *ApJS*, 151, 35
- Goto, M., *et al.* 2007, *ApJ*, 662, 389
- Habart, E., Natta, A., & Krügel, E. 2004, *A&A*, 427, 179
- Hobbs, L. M., *et al.* 2008, *ApJ*, in press
- Hollis, J. M., Lovas, F. J., Jewell, P. R., & Coudert, L. H. 2002, *ApJ* (Letters), 571, L59
- Hudgins, D. M., & Allamandola, L. J. 1999, *ApJ* (Letters), 516, L41
- Hudgins, D. M., Bauschlicher, C. W., & Allamandola, L. J. 2005, *ApJ*, 632, 316
- Hudson, R. L., & Moore, M. H. 2000, *Icarus*, 145, 661
- Imanaka, H., *et al.* 2004, *Icarus*, 168, 344
- Jaeger, C., Molster, F. J., Dorschner, J., Henning, Th., Mutschke, H., & Waters, L. B. F. M. 1998, *A&A*, 339, 904
- Jaeger, C., Dorschner, J., Mutschke, H., Posch, Th., & Henning, Th. 2003, *A&A*, 408, 193
- Jaeger, C., *et al.* 2006, *ApJS*, 166, 557
- Jones, A. P., Tielens, A. G. G. M., & Hollenbach, D. J. 1996, *ApJ*, 469, 740
- Kissel, J. & Krueger, F. R. 1987, *Nature*, 326, 755
- Kobayashi, H., Kawakita, H., Mumma, M. J., Bonev, B. P., Watanabe, J., & Fuse, T. 2007, *ApJ* (Letters), 668, L75
- Kwok, S. 2007a, *Adv. Space Res.*, 40, 655
- Kwok, S. 2007b, *Adv. Space Res.*, 40, 1613
- Lahuis, F., *et al.* 2006, *ApJ* (Letters), 636, L145
- Linnartz, H., *et al.* 2000, *J. Chem. Phys.*, 112, 9777
- Lucas, R. & Liszt, H. S. 2000, *A&A*, 358, 1069
- Maier, J. P., Walker, G. A. H., & Bohlender, D. A. 2004, *ApJ*, 602, 286
- Marcelino, N., Cernicharo, J., *et al.* 2007, *ApJ* (Letters), 665, L127
- Markwick, A. J., Ilgner, M., Millar, T. J., & Henning, Th. 2002, *A&A*, 385, 632
- Matthews, C. N., & Minard, R. D. 2006, *Faraday Disc.*, 133, 393
- McCarthy, M. C., Gottlieb, C. A., Gupta, H., & Thaddeus, P. 2006, *ApJ* (Letters), 652, L141
- Mennella, V., Baratta, G. A., Colangeli, L., Palumbo, M., Rotundi, A., Bussoletti, E., & Strazzulla, G. 1997, *ApJ*, 481, 545
- Messenger, S., Nakamura-Messenger, K., Keller, L., Matrajt, G., Clemett, S., & Ito, M. 2007, *Geochimica et Cosmochimica Acta*, 71, 15
- Muñoz-Caro, G. M., Ruiterkamp, R., Schutte, W. A., Greenberg, J. M., & Mennella, V. 2001, *A&A*, 367, 347
- Muñoz-Caro, G. M. & Schutte, W. A. 2003, *A&A*, 412, 121
- Muñoz-Caro, G. M., *et al.* 2006, *A&A*, 459, 147
- Niemann, H. B., *et al.* 2005, *Nature*, 438, 779
- Öberg, K. I. *et al.* 2007, *ApJ* (Letters), 662, L23
- Öberg, K. I. *et al.* 2008, *ApJ*, 678, 1032
- Pendleton, Y. J. 2004, in: A. Witt *et al.* (eds.), *Astrophysics of Dust*, (ASP Vol. 304), p. 573
- Pendleton, Y. J., & Allamandola, L. J. 2002, *ApJS*, 138, 75
- Pety, J., *et al.* 2005, *A&A*, 435, 885
- Posch, Th., Baier, A., Mutschke, H., & Henning, Th. 2007, *ApJ*, 668, 993
- Rouille, G., *et al.* 2007, *J. Chem. Phys.*, 126, 174311
- Ruiterkamp, R., *et al.* 2005, *A&A*, 432, 515
- Sandford, S. A., *et al.* 2006, *Science*, 314, 1720
- Schilke, P., Benford, D. J., Hunter, T. R., Lis, D. C., & Phillips, T. G. 2001, *ApJS*, 132, 281
- Sloan, G. C., *et al.* 2005, *ApJ*, 632, 956
- Smith, I. W. M., Sage, A. M., Donahue, N. M., Herbst, E., & Quan, D. 2006, *Faraday Discussions*, 133, 137
- Snow, T. P., & McCall, B. J. 2006, *ARA&A*, 44, 367
- Song, I.-O., Kerr, T. H., McCombie, J., & Sarre, P. J. 2003, *MNRAS* (Letters), 346, L1
- Tan, K. F., & Salama, F. 2005, *J. Chem. Phys.*, 123, 14312
- Tielens, A. G. G. M. 2008, *ARA&A*, in press
- van Winckel, H., Cohen, M., & Gull, T. R. 2002, *A&A*, 390, 147

- van Hemert, M. C. & van Dishoeck, E.F. 2008, *Chem. Phys.*, 343, 292
Visser, R., *et al.* 2007, *A&A*, 466, 229
Watanabe, N., Nagaoka, A., Shiraki, T., & Kouchi, A. 2004, *ApJ*, 616, 638
Wyrowski, F., Schilke, P., Walmsley, C. M., & Menten, K. M. 1999, *ApJ* (Letters), 514, L43
Yan, L., *et al.* 2005, *ApJ*, 628, 604

Discussion

MUMMA: Would you comment on the role of the X-ray processing around young stars, in particular through the enhanced ion-molecule processing such as H_3^+ .

VAN DISHOCK: There is no doubt that young stars have X-rays and in fact you can even measure them. We know that the surfaces and interiors of a number of protoplanetary disks are exposed to X-rays. Any enhanced ionization rate will enhance H_3^+ and drives ion-molecule chemistry. However, to what extent that it will lead to complex organics is not certain. Of course too strong X-ray emission is not good because it will destroy the more volatile organic molecules. In the inner parts of the disks, it will be very difficult for small PAHs to survive there.

VAIDYA: What is against graphite as the carrier of the 2175 feature?

VAN DISHOCK: There is not much spectroscopic evidence because we just have one very broad feature. I have always felt that some form of graphite must be present, but exactly what the carrier is, is difficult to answer.



Michael Mumma, Ruud Visser, and Ewine Van Dishoeck having a lively discussion during the coffee break (photo by Dale Cruikshank).



The Loke Yew Hall.